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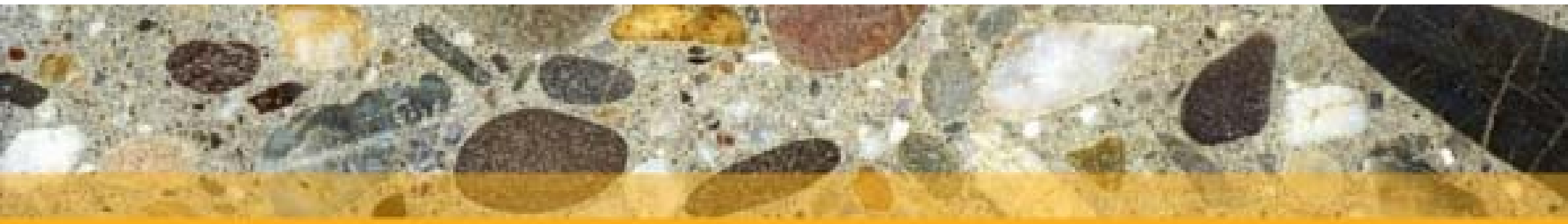

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A step ahead in understanding effects of admixtures

On the track of the interactions between cement and concrete admixtures

The use of concrete admixtures to control the properties of fresh and hardened concrete is state of the art today. In this field the interaction between cement and admixtures is very important. Investigations were undertaken to find out the cement properties influencing the behaviour of admixtures and those of admixtures influencing cement hydration.

Nearly 90 % of concretes contain concrete admixtures. The influence that concrete admixtures have on the hydration of cement is most often determined empirically and forms the subject of controversial discussions. There is still a substantial lack of scientifically based understanding of the precise working mechanisms of some admixtures. This applies to superplasticizers on the basis of polycarboxylate ether, long-term retarding admixtures, shrinkage reducing admixtures, and novel air-entraining concrete admixtures in particular, the function of which formed the subject of extensive investigations.

Superplasticizers

The Research Institute has investigated the effects of concrete plasticizing admixtures and the adjustment of the consistency of concrete using superplasticizers over the last few years. The work is continuing with investigations of superplasticizers of the "new generation" based on polycarboxylate ethers. The advantage in using these new superplasticizers is the fact that to the electrostatic repulsion by the transfer of positively charged surfaces (due to the sorption of the dissociated main chains of the polymers) a sterical repulsion is added because of the additional side chains. By adding a stabilizer, a further increase in the flowability can be achieved, since glide surfaces are being created at the interfaces between the individual solid particles which will further decrease the inner friction of the suspension (tribological effect). **Fig. 1** illustrates this effect in a schematic presentation. First hydration products can grow in the space between two sterically divided cement grains, without substantially influencing the movement of the suspension. A strong initial plasticizing and/or prolonged workability period of fresh concrete can be adjusted by varying the length ratio of the main chains to the side chains. The effectiveness of these superplasticizers and the influence of reactivity, grain size distribution and volume proportion of the solid particles in the suspension, as well as the surrounding temperatures, are being investigated by extensive research work in the Research Institute of the Cement Industry.

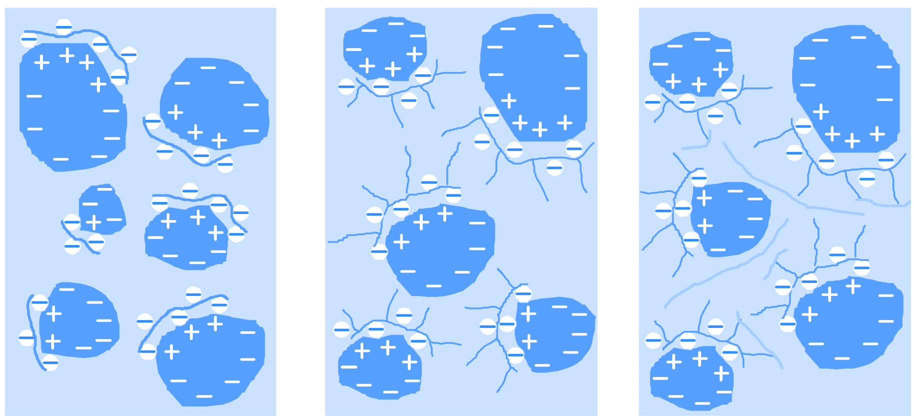
Shrinkage reducing admixtures

Concrete shrinkage leads to deformation that may cause stress in structural elements in case of constraint. As a consequence, cracks that impair durability may occur. Shrinkage is induced by fluctuations in the moisture content of concrete, which change the interior forces in the microstructure of the hardened cement paste matrix as a consequence of the environmentally induced or internal desiccation of the concrete. This results in tensile stress, which causes the matrix to contract. Deformation is impeded by the aggregates to some degree.

Shrinkage Reducing Admixtures (SRA) were developed in Japan in the early eighties to reduce concrete shrinkage. The use of SRA in standard concrete was found to reduce shrinkage by up to 50% depending on the w/c ratio and the age of the concrete. At the same time, compressive strength and tensile strength decreased.

Shrinkage reducing admixtures are water-soluble, surface-active agents. They primarily consist of higher-grade alcohol which reduces the surface tension of water.

Research results published to date show that the statements on



Electrostatic effect melamine- and naphthaline-sulfonates (SP)	Electrostatic and steric effect polycarboxylate ether (SP)	Electrostatic, steric and tribologic effect polycarboxylate ether (SP) in combination with stabilizers (VEA)

Fig. 1: Schematic representation of the action mechanisms of concrete plasticizing admixtures

the working mechanisms and effects of SRA are contradictory. Therefore a research project is aimed at identifying the fundamental workings of shrinkage reducing admixtures and their interactions with cement.

First results show, that SRA quantities between 10 and 20 wt. % relative to the water content reduce the surface tension of the mixing water up to 60 %. Higher dosages do not reduce the surface tension of the aqueous solutions any further. The autogeneous and basic shrinkage of cement paste can be reduced up to 50%. The reduction of shrinkage strongly depends on the active substance and the age of specimens **(Fig. 2)**, the w/c ratio and the SRA amount added. Furthermore SRA reduces not only the surface tension of the pore solution, but they also influence the pore size distribution of the hardened cement paste.

Air-entraining agents

Concrete with resistance to freeze-thaw with de-icing salt must have, besides an adequate dense hardened cement paste and aggregate with high freeze-thaw resistance, an air-entraining agent which generates a sufficient quantity of small air voids in the hardened concrete.

The basic materials are soaps made from natural resin (wood resin) and synthetic active ingredients (e. g. alkylpolyglycolether, alkyl sulfate or alkyl sulfonate). They act in the interface between air and water and lower the surface tension of the mixing water. This enhances the generation of small bubbles, which are stabilized by the air-entraining agent. During the mixing process, the molecules arrange around air bubbles. The polar hydrophylic group faces towards the water while the hydrophobic chain is oriented towards the air in the bubble. Another part of the molecules are sorbed with the normally negative charged polar group by positively charged areas of the cement particles **(Fig. 3)**.

The type of the active ingredient of the air-entraining agent influences the formation of air voids. Synthetic tensides lead to smaller pores than natural resins, but they need a longer mixing time until they are activated. Also the type of cement influences the air content. Two main aspects are the alkali content and the fineness of the cement. The air content increases with increasing alkali content. With increasing specific surface of the cement, the air content decreases. If Portland-fly ash cement is used, the air content decreases with increasing content of fly ash. The amount is influenced by the carbon content of the fly ash. The carbon absorbs the air-entraining agent thus preventing it from stabilizing air bubbles in fresh concrete. Regarding Portland slag and blast furnace cements, the quantity of the air-entraining-agent is a function of the fineness and the content of blast furnace slag used. The air content decreases with increased fineness and content of blast furnace slag in

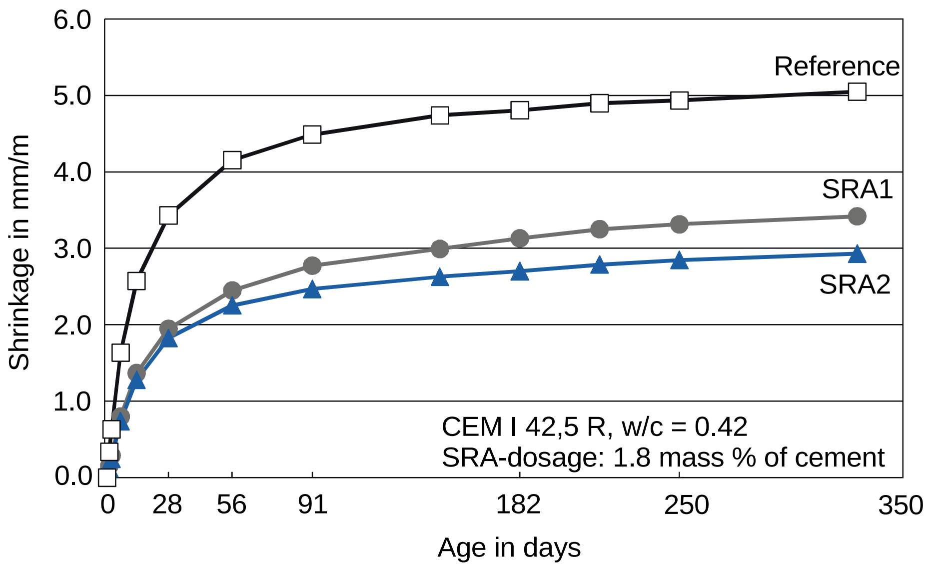


Fig. 2: Shrinkage of hardened cement paste in dependency of the active agent of the shrinkage reducing admixture and hydration time

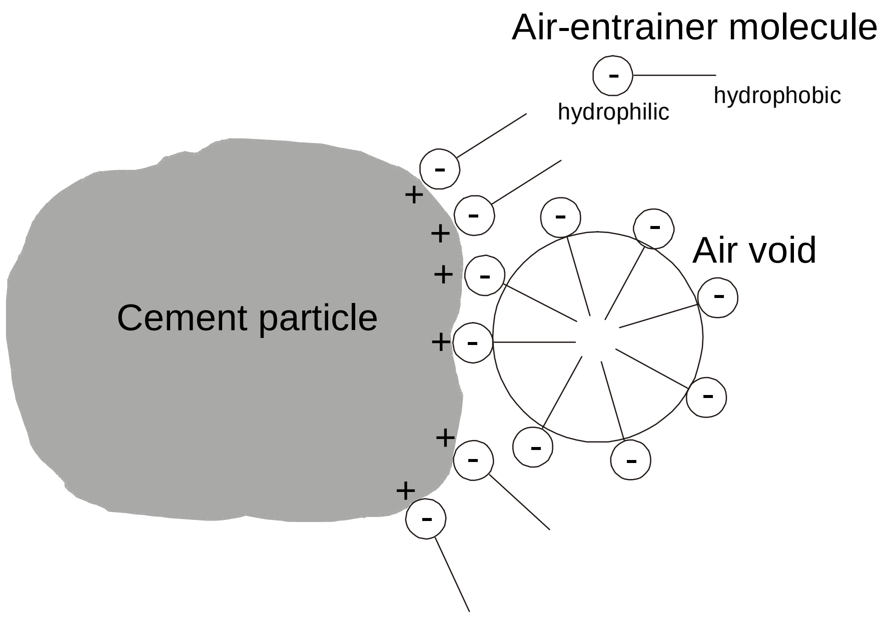


Fig. 3: Sorption of the air-entrainer molecules and adhesion of an air void to a cement particle

the cement. The use of Portland limestone cement has practically no effect on the air content.

By reason of a damage due to a very high air void content of the hardened road paving concrete investigations were run in the Research Institute with six ordinary air-entrainers – three based on synthetic active (S1, S2, S3) and three based on natural active agents (N1, N2,N3, **Fig. 4**). The air void formation was determined as a function of mixing time with the quantity AEA determined in a preliminary test to achieve an air content of about 5 vol.-% (normal quantity) and the double quantity. The test results showed, that a substantial increase in air content can only happen in case of double dosage. Due to a very short mixing time at the job site, an excessive quantity of air-entrainer was metered during production to attain the desired air content. In that case, the fresh concrete is supplied with air-entrainer which is not sufficiently decomposed and activated. The air void content may increase due to a subsequent mixing process during placing, e. g. by spreading and vibrating the concrete. It was not possible to assign the different behaviour of the air-entrainers systematically to certain types of active agents. This shows that the knowledge about the working mechanisms of air-entraining agents is insufficient. A research project is therefore determining the interactions between the active agent forming air voids, mixing time and quantity added.

As air-entrainers often consist of a mix of different substances, pure chemicals are in the investigations included as well as ordinary air-entrainers. To define the sorption behaviour of the air-entrainers, flotation tests are very suitable. Water, cement and air-entrainer were mixed in a vessel and fine air bubbles were injected into the suspension. When air-entrainer molecules

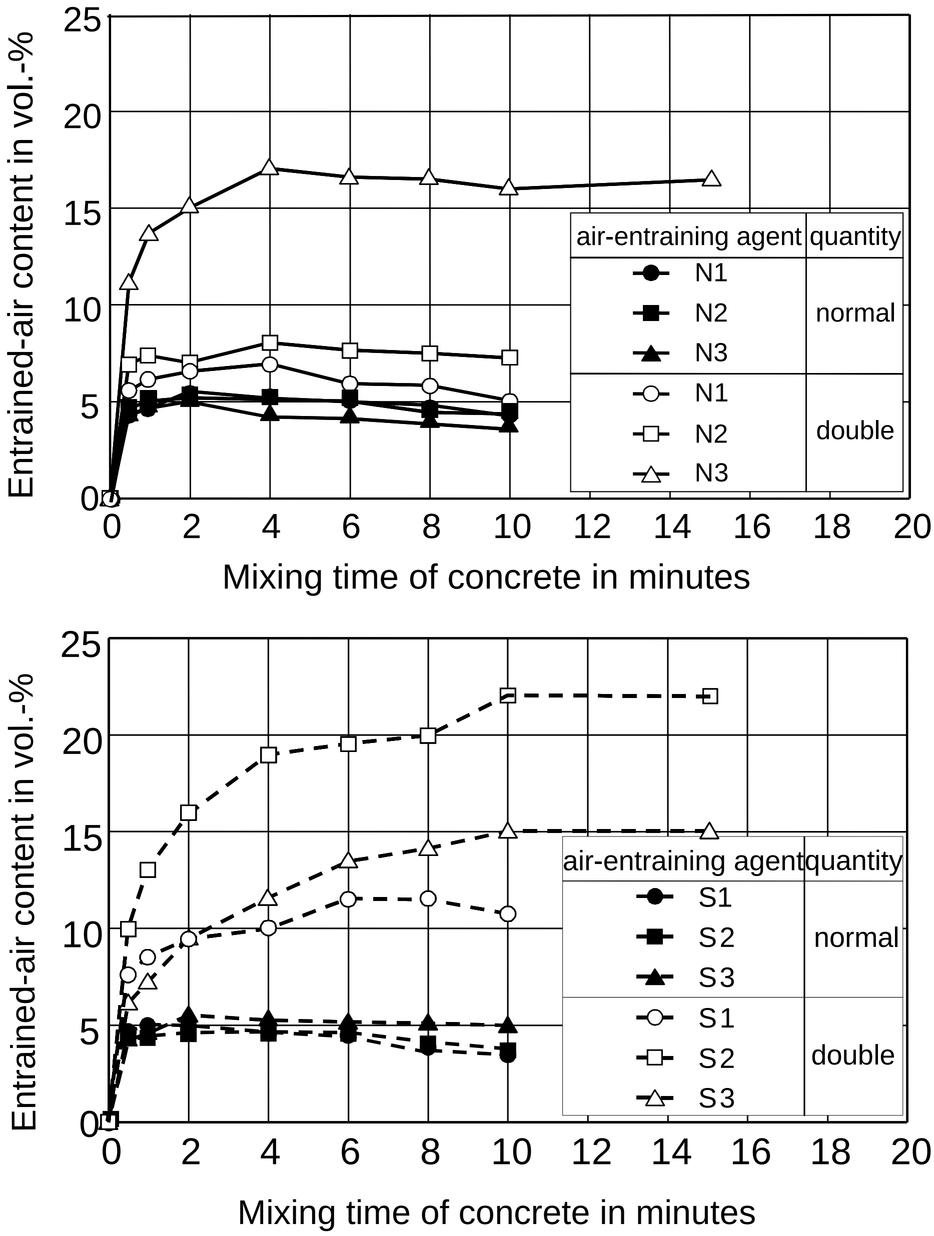


Fig. 4: Voids formation as a function of mixing time, type of active agent and quantity of air entrainer added

are sorbed by cement particles, air bubbles adhere and rise to the water surface with the cement particles. The quantity of cement floated can be determined. The investigations covered two ordinary air entraining agents on the basis of a natural and a synthetic active agent with different quantities added. With the air-entrainer based on synthetic active agents, the quantity of floated cement rises continually as the quantity added is increased. With the air-entrainer based on root resin, by contrast, the proportion of floated cement stops increasing once a certain quantity added is reached. With the air-entrainer based on synthetic agent, a larger share of the air-entrainer molecules added remains dissolved. As a consequence, more air bubbles can be stabilised, which can in turn adhere to cement particles and hence increase the share of floated cement.

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